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Interlaminar Shear Property of Modified Glass Fiber-reinforced Polymer with Different MWCNTs

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Abstract

The interlaminar shear property of composites remains a serious concern in application. In this article, five different multiwalled carbon nanotubes (MWCNTs) are tried to improve the interlaminar shear property of composites, including two MWCNTs (MWCNTs-A and MWCNTs-B) different with diameters and lengths, an orientated MWCNTs (MWCNTs-C), a film-shaped MWCNTs-A (MWCNTs-D), and a surface-treated MWCNTs-B (MWCNTs-E). The interlaminar shear strength (ILSS) of the composites, filled with one of the above-mentioned materials as a constituent is investigated. The best ILSS increases by 8.16% from 24.5 MPa to 26.5 MPa with MWCNTs-E. In addition, the dispersion of MWCNTs in a glass fiber-reinforced polymer (GFRP) is researched by a scanning electron microscopy (SEM) in association with the ILSS results.

Keywords: MWCNTs; ILSS; microstructure; GFRP

1 Introduction

Carbon nanotubes (CNTs), a new form of crystalline carbon, are of two types: single-walled (SWCNTs) and multiwalled (MWCNTs). With their mechanical and physical properties suitable for wide applications, in recent years, they have become an important subject in which many researchers are engaged. Compared with high performance carbon fibers, CNTs have the ability to combine high modulus and tensile strength[1]. The elastic modulus ranges from 500 to 1 000 GPa and the tensile strength from 50 to 100 GPa[1], which make CNTs ideal candidate for producing the next generation of composites. The CNTs-based composites have been intensively studied by using different matrix materials, such as polymers[2-6], ceramics[7-9], and metals[10]. Many books and articles have been published on the mechanical properties of the CNTs-modified resin matrix.

Breton[11] dispersed different types of catalytically grown MWCNTs in an epoxy resin, and then tested the mechanical properties of the MWCNTs/epoxy composites. The results demonstrated that the epoxy resin with 1 wt%, 3 wt% or 6 wt% MWCNTs acquired a higher tensile modulus. Zhou[12] studied the CNTs loading effects on the mechanical properties of composites with unfilled as well as 0.1 wt%, 0.2 wt%, 0.3 wt%, and 0.4 wt% CNTs-filled epoxy, respectively. The results showed that the modulus increased with higher CNTs-content and the 0.3 wt% CNT-filled system reached the maximum strength. By Allaoui's[13] study, the composite containing 1 wt% MWCNTs had the elastic modulus and a yield strength double that of the pure resin matrix, whereas, the composite containing 4 wt% MWCNTs was even quadruple.

However, to date, there are few studies on the interlaminar shear property of CNTs-modified resin

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matrix composites and, in fact, the problem about interlaminar shear property is still nowhere near settled. If CNTs can disperse between the fiber fabric layers in the thickness direction of the composites, the CNTs that are preferentially orientated between the glass fiber layers in the thickness direction can lead to the interpenetration of CNTs and the fiber fabric, thus forming a new interface between the resin and fiber fabric, to transfer the load from the matrix to the fiber reinforcement, more effectively. This results in the enhanced interlaminar shear strength (ILSS) of the composite.

This study compares five MWCNTs with different morphologies in terms of the influences of their characteristics (diameter, length, surface morphology) on the dispersion within the composites and the ILSS of MWCNTs-modified glass fiber-reinforced polymer (GFRP), and tries to improve the interlaminar shear property of the MWCNTs-modified GFRP.

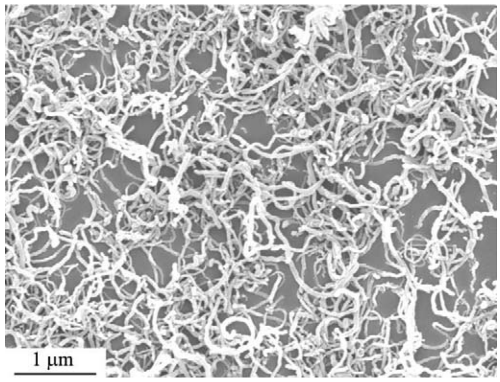
2 Experimental

2.1 Materials

A 840s epoxy (EP) resin system, procured from Wuxi Edison Epoxy Co. Ltd., was used as the resin matrix and 2-ethyl-4-methyl imidazole from Tianjin Chemistry Reagents Co. Ltd. was used as curing agent in this study. The plain weave glass fabric 0.16 mm thick from the Nanjing Glass fiber Research & Design Institute acted as the reinforcement. Three types of MWCNTs (MWCNTs-A, MWCNTs-B, and MWCNTs-C) served as interlaminar-reinforcements. In order to further improve the interlaminar shear property of the GFRP, two new MWCNTs were prepared by special treatments. MWCNTs-A were fabricated into a film shape about 0.25 mm thick, by using a filtrating process and labeled as MWCNTs-D, and MWCNTs-B were subjected to a surface treatment by using a mixture of H_2SO_4 and HNO_3 in a volumetric proportion of 3:1 for one hour, at 80 °C, and marked as MWCNTs-E. Table 1 shows other information about MWCNTs and Figs.1-5 their morphology.

Table 1 Dimension and characteristics of MWCNTs

The type of MWCNTs	Diameter	Length	Producer
MWCNTs-A	10-30 nm	5-15 μm	Shenzhen Nano Port Co. Ltd.
MWCNTs-B	40-60 nm	1-2 μm	Tsinghua University
MWCNTs-C (Orientated MWCNTs)	40-60 nm	1-2 mm	Tsinghua University
MWCNTs-D	Film of MWCNTs-A		
MWCNTs-E	A surface treatment applied to MWCNTs-B		



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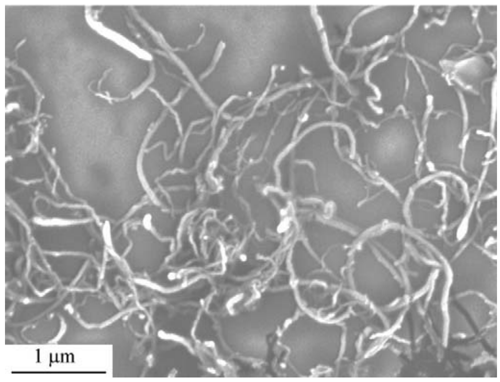
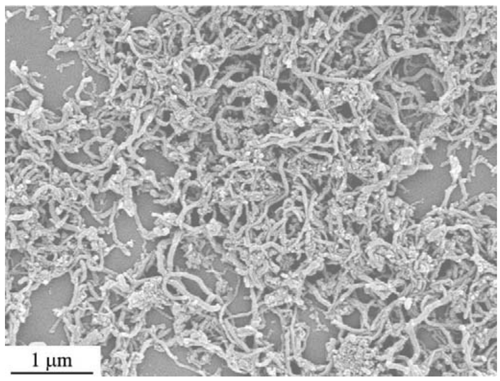


(b)

Fig.1 Morphology of MWCNTs-A.



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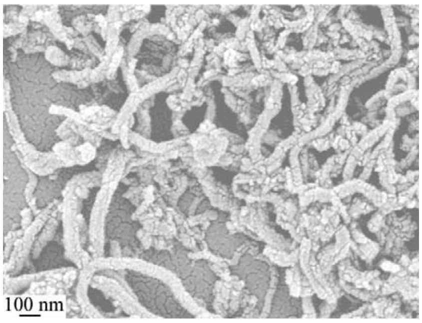

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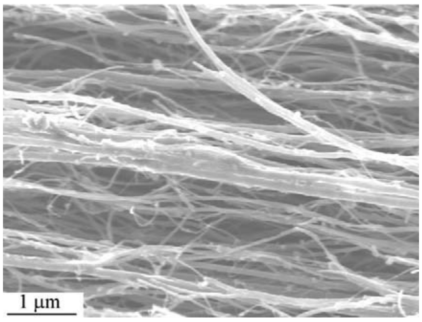
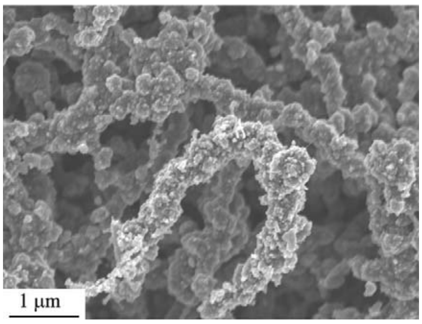
Fig.2 Morphology of MWCNTs-B.

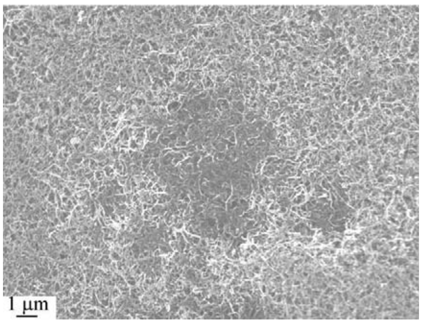


(a) The orientation of diameter

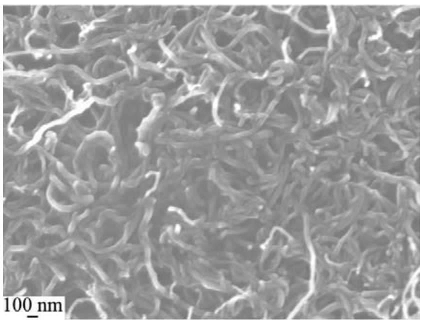


(b) The orientation of top

Fig.3 Morphology of MWCNTs-C.

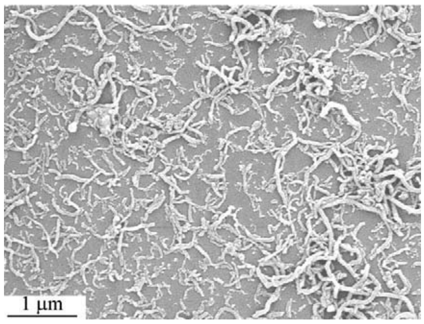


(a)



(b)

Fig.4 Morphology of MWCNTs-D.



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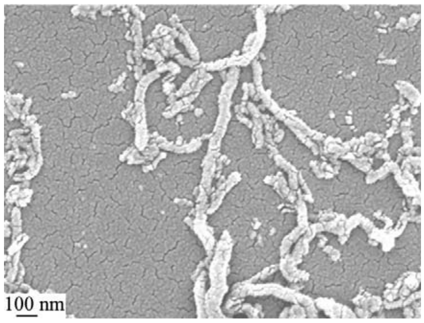


(b)

Fig.5 Morphology of MWCNTs-E.

2.2 Dispersion and compression molding process

As mentioned in many articles[14-15], the problem of dispersion of MWCNTs in the resin matrix remains unsettled as yet. In many experiments, minicalander or ultrasonic agitation was used to disperse MWCNTs because of their high shear forces. In this study, MWCNTs-A, MWCNTs-B and MWCNTs-E were mixed into the epoxy resin directly in a certain proportion, after which the epoxy/MWCNTs suspension was dispersed under both ultrasonic agitation and mechanical excitation at 80 °C, for one hour. MWCNTs-C and MWCNTs-D were used directly as interlaminar-reinforcements in a manner similar to the preforms usually used in composites because they had already been converted into micro-films or micro-pieces.

After dispersion of MWCNTs in the epoxy matrix, the GFRPs were produced in a compression molding process, where MWCNTs-A, MWCNTs-B and MWCNTs-E were used as interlaminar-reinforcements. Subsequently the material was retained in the mold on a block press and cured for 1 h, at 70 °C. Following that, the laminates were post-cured at 120 °C for 2 h. The glass fiber-content in the GFRPs was 20 vol% with six glass fiber layers and the MWCNTs-content was 3 wt% in epoxy matrix. When MWCNTs-C were used as an interlaminar-reinforcements, the glass fiber-content of the GFRPs was still controlled to be 20 vol%. The MWCNTs-C content was 12 wt% and only one layer of orientated MWCNTs was inserted in the middle of the six glass fiber layers. When MWCNTs-D was used as an interlaminar-reinforcement, the glass fiber-content of the GFRPs was controlled to be 15.7 vol%. The layup design of MWCNTs-D/GF/EP laminates was so conducted that five glass fiber layers and four MWCNTs films were laid alternately with 40 wt% MWCNTs-D. The molding process was similar to the above-mentioned.

2.3 Characterization of interlaminar shear property

The ILSS of the MWCNTs/GF/EP laminates was measured according to ASTM D-2344 using the short-beam method. Fig.6 shows short-beam test specimen configurations and the horizontal shear load scheme. A MTS 880 universal tensile testing machine was used to determine the ILSS. At least five specimens were tested when MWCNTs-A, MWCNTs-B, MWCNTs-D, and MWCNTs-E were used as interlaminar-reinforcements. The results were averaged and the standard error was calculated. Only one specimen was tested when MWCNTs-C (orientated MWCNTs) were used as the interlaminar-reinforcement because of the limited amount of available MWCNTs-C.

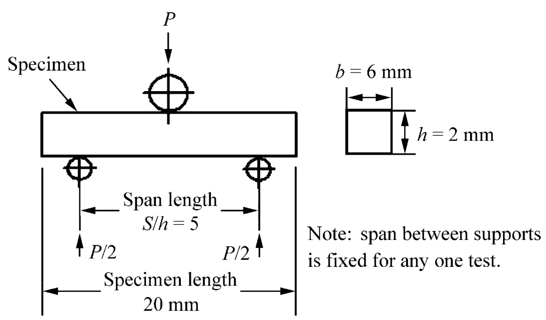


Fig.6 Short-beam test specimen configurations and horizontal shear load diagram.

2.4 Electron microscopy

Jeol JSM-SEM 6700 and Leo FE-SEM 1530 were followed to obtain scanning electron microscopy (SEM)-micrographs of the composite laminates and raw materials. The samples were investigated at acceleration voltages between 3 kV and 10 kV.

3 Results and Discussion

3.1 Interlaminar shear property of modified GFRPs with MWCNTs

As an important parameter and a main designation, the ILSS characterizes the interlaminar property of composite laminates. Since the failure of a composite often occurs on the interface, improving the interface bonding strength becomes an urgent need. This article aims at investigating the variation of the interlaminar shear property of composite laminates with MWCNTs functioning as interlaminar-reinforcements. The ILSS was determined by short-beam tests.

Table 2 shows the ILSS of the MWCNTs (MWCNTs-A, MWCNTs-B and MWCNTs-E)/GF/EP laminates with 20 vol% of glass fiber and 3 wt% of MWCNTs in epoxy resin with the standard error. Table 3 the ILSS of MWCNTs-C/GF/EP with 20 vol% of glass fiber and 12 wt% of MWCNTs in epoxy resin. Table 4 the ILSS of MWCNTs-D/GF/EP with 15.7 vol% of glass fiber and 40 wt% of MWCNTs in epoxy resin with the standard error. Fig.7 compares the ILSS of different specimens.

It can be seen that almost all epoxy matrices with MWCNTs directly dispersed in them, exhibit increased ILSS, of which MWCNTs-E achieves the highest, up by 8.16% from 24.5 MPa to 26.5 MPa.

Table 2 The ILSS results of MWCNTs/GFRP laminates

Unit: MPa

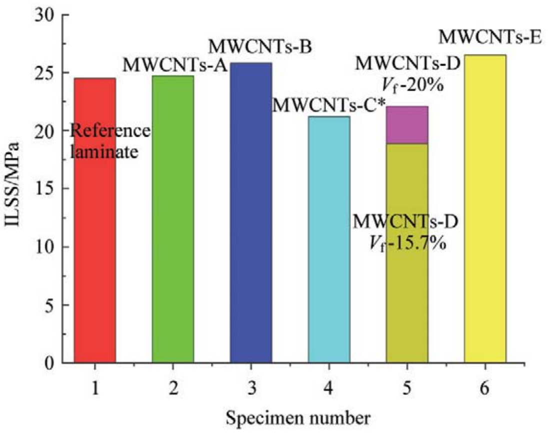
No.	Laminate			
	Reference	MWCNTs-A/GFRP	MWCNTs-B/GFRP	MWCNTs-E/GFRP
1	24.1	24.8	27.1	26.0
2	25.0	24.3	24.7	25.2
3	25.8	25.0	24.3	24.8
4	24.1	24.2	27.2	26.6
5	23.7	25.0	25.7	29.9
Average ILSS	24.5	24.7	25.8	26.5
CV%	3.48	1.57	5.17	7.64

Table 3 The ILSS results of MWCNTs-C/GFRP laminates

Type of specimen	Reference laminates	MWCNTs-C /GFRP laminate
ILSS/MPa	24.5 (average)	21.2

Table 4 The ILSS results of MWCNTs-D/GFRP laminates
Unit: MPa

No.	Reference laminates	MWCNTs-D/GFRP laminates
1	22.0	20.1
2	20.1	18.5
3	19.3	18.3
4	25.3	18.4
5	20.3	19.3
Average ILSS	21.4	18.9
CV%	11.18	4.07



Note: ∗–one specimen was tested when MWCNTs-C was used as an interlaminar-reinforcement because of the limited amount of available MWCNTs-C. The data for MWCNTs-C shown here are only for reference.

Fig.7 The ILSS results of MWCNTs/GF/EP composite laminates containing 20 vol% of glassfibres.

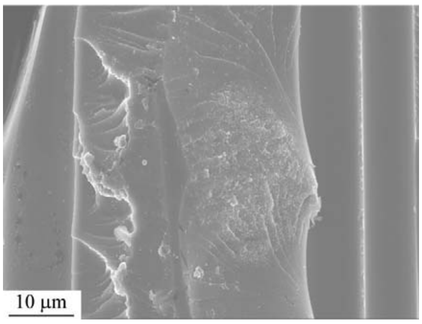
The ILSS of MWCNTs-C/GF/EP composite laminates decreases obviously by 13.5 % from 24.5 MPa down to 21.2 MPa. The same is the case with MWCNTs-D/GF/EP, which decreases by 9.8%, from 24.5 MPa down to 22.1 MPa. The data for MWCNTs-D/GF/EP composite laminates containing 20 vol% of glass fiber are converted from the ILSS of MWCNTs-D/GF/EP containing 15.7 vol% of glass fiber, according to the mixture rule. Table 4 shows the ILSS measured in the experiments.

3.2 Microstructure of interlaminar-reinforced GFRP with MWCNTs

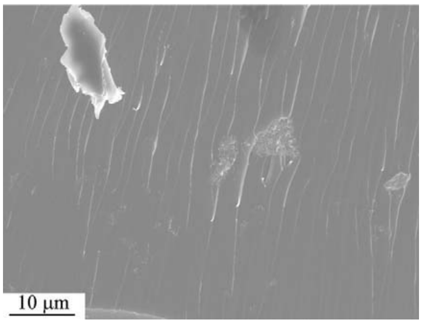
The small size of MWCNTs in the nanometer order and their high specific surface area (SSA) produce enormous attractive forces between the nano-particles. This results in the reagglomeration of MWCNTs and prevents them from homogeneous dispersion in the epoxy matrix.

The experiment demonstrates that most of the MWCNTs that disperse in the epoxy matrix as interlaminar-reinforcements reagglomerate. Fig.8 shows the SEM-micrographs of MWCNTs-A, MWCNTs-B, and MWCNTs-E/GF/EP composite laminates. From this, it can be observed that no matter what type of MWCNTs are used, a large number of agglomerates called “spot-structures” distribute in the matrix between the glass-fabrics, with only a few MWCNTs that disperse homogeneously, as shown in Fig.9.

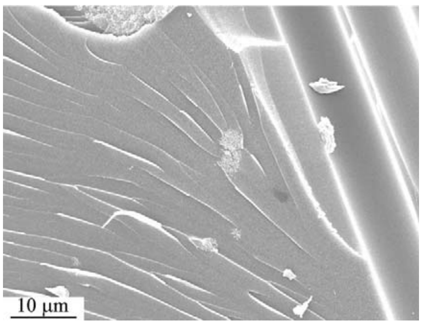
From Fig.8, it is noted that all the MWCNTs do not disperse well in the matrix, but reagglomerate, as is the case with MWCNTs-A, MWCNTs-B,



(a) MWCNTs-A

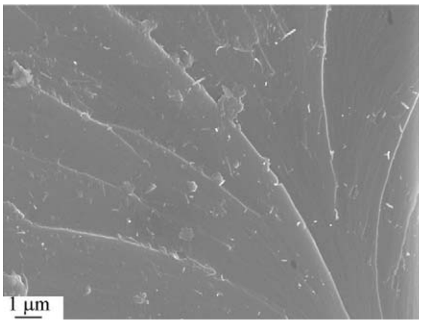


(b) MWCNTs-B

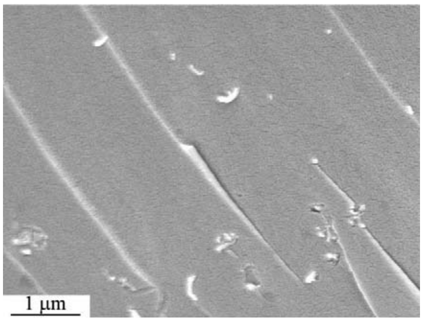


(c) MWCNTs-E

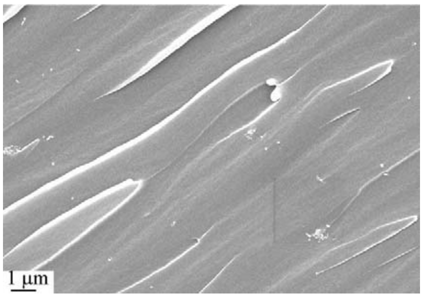
Fig.8 Reagglomeration of MWCNTs in epoxy matrix.



(a) MWCNTs-A



(b) MWCNTs-B



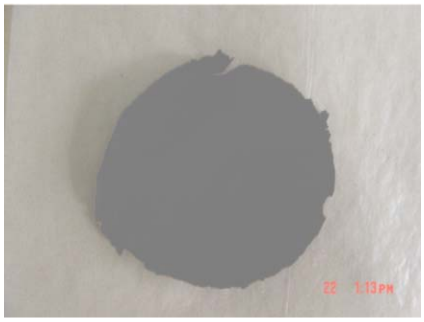
(c) MWCNTs-E

Fig.9 MWCNTs distributing homogeneously in epoxy matrix.

MWCNTs-E, and most MWCNTs. Although no noticeable difference exists between the three types of MWCNTs, the size of their "spot-structures" is not the same with the MWCNTs-A being the biggest and the MWCNTs-E the smallest. This difference contributes to the dispersion of MWCNTs-E better than MWCNTs-B and MWCNTs-A, which results in the highest ILSS coming off the MWCNTs-E-modified GFRP. Moreover, from Fig.2 and Fig.5, it can be seen that the length of MWCNTs-E is shorter than that of MWCNTs-B and the surface is rougher than that of MWCNTs-B, which makes the interface bonding strength of MWCNTs-E higher than that of MWCNTs-B consequently leading to a higher ILSS of MWCNTs-E-filled composite laminates. The longest and thinnest of the three types of MWCNTs, MWCNTs-A have the highest SSA, thus forming an enormous amount of attractive forces between nanotubes, which causes very serious reagglomeration, exerting the least effect on the reinforcement. On the other hand, as shown in Fig.9 no matter what type of MWCNTs are used, only a small amount of MWCNTs distribute homogeneously in the epoxy matrix, which results in minimal intensifying effects on interlaminar shear property. Therefore, improved as it is, ILSS has a relatively small room for improvement.

When MWCNTs-C and MWCNTs-D were used as interlaminar-reinforcements, the dispersion problem was solved because MWCNTs-C had already grown according to the determined orientation and the MWCNTs-D had been worked on and fabricated into a macro-film before the composite laminates were fabricated as shown in Fig.10.

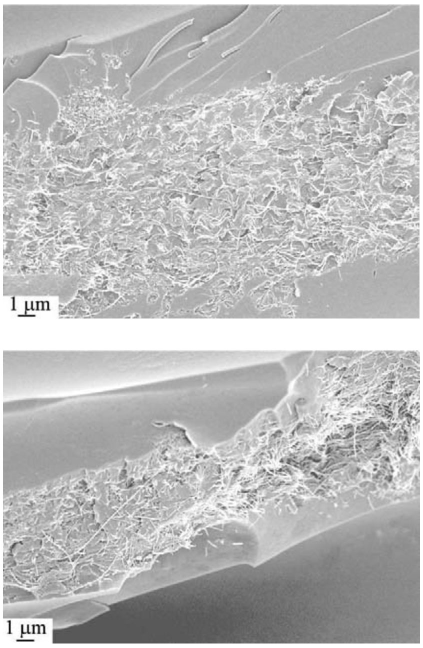
(a) MWCNTs-C



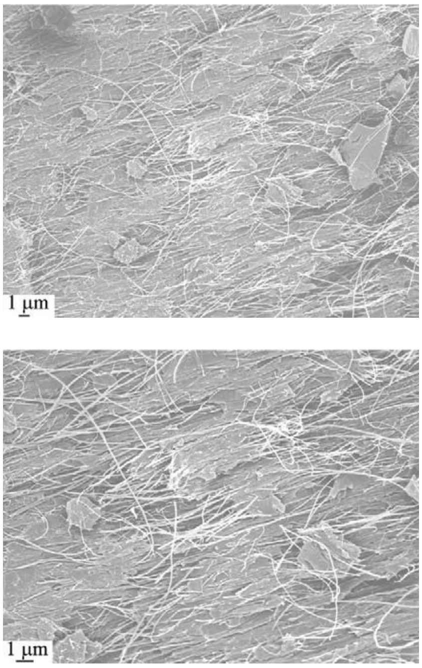
(b) MWCNTs-D

Fig.10 Macroscopical morphology of MWCNTs-C and MWCNTs-D.

Fig.11 and Fig.12 show the SEM-micrographs of MWCNTs-C/GF/EP and MWCNTs-D/GF/EP composite laminates. It is clear that the homogeneously distributed MWCNTs-C and MWCNTs-D permeate all over the composite laminates. Moreover, the orientation of MWCNTs-C has been settled basically vertical to the layer of laminate.

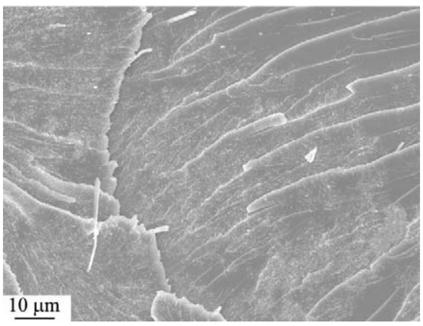


(a) Orientation of top



(b) Orientation of diameter

Fig.11 SEM-micrograph of MWCNTs-C/GF/EP.



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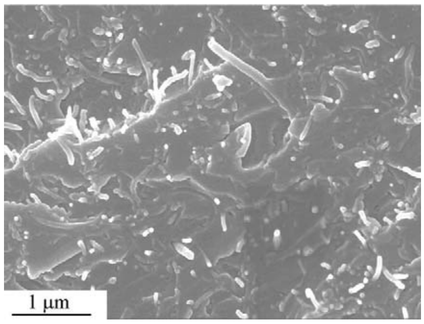

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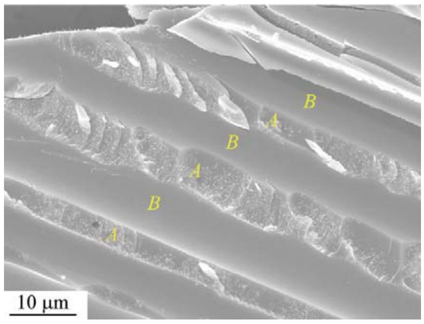

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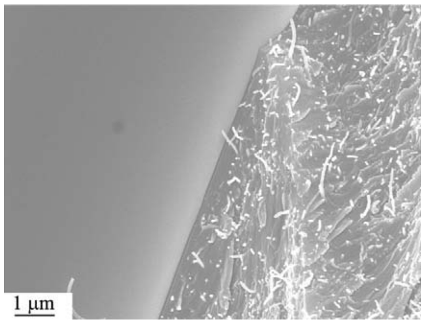

(d)

Fig.12 SEM-micrograph of MWCNTs-D/GF/EP.

The ILSS of MWCNTs-C/GFRP is not improved, but decreases by 13.5% instead. From Fig.11(c) and (d), it can be seen that the surface of MWCNTs is almost not saturated by the epoxy resin matrix because the orientated MWCNTs (MWCNTs-C) are so closely clumped together that the resin is hardly able to penetrate into between. Besides, it would have been expected that the upstanding tops of orientated MWCNTs could insert into the bundles of glass fiber and as such lead to the inter-penetration of MWCNTs and glass fiber fabric, to resist the interfacial shear failure and enhance the ILSS. In fact, from Fig.3(b) it is seen that the tops of MWCNTs-C do not stand up straight, but tangle up with each other, failing to insert into the bundles of glass fiber to realize the interpenetration of MWCNTs and glass fiber fabric. As a consequence of this, any increase in ILSS can not come into effect as hoped and the composite laminate becomes a sandwich-like structure inclusive of three-phases: an epoxy matrix and two reinforcements, including an orientated MWCNTs layer and glass fiber layers. Moreover, this would even induce negative effects, as the tangled tops of MWCNTs could hinder the epoxy resin from penetrating in between the MWCNTs, and could make the MWCNTs-C inadequately saturated by the resin matrix. As a remedy, an extra treatment such as laser cutting can be used to achieve upstanding tops in the orientated MWCNTs-C. In addition, from Fig.3(a) and (b), it can be seen that the surface of MWCNTs-C does not look slippery, as a large amount of gelatiniform substance can be observed on it. These are probable by-products left behind during the growing process of carbon nanotubes. This substance acts as defects to decrease the interfacial shear property of composite laminates. The amelioration of production process of orientated MWCNTs will form the focus of the further study.

The ILSS of MWCNTs-D-modified GFRP also decreases as shown in Fig.7. From Fig.12(a) and Fig.12(b), it can be seen that MWCNTs-D disperse homogeneously in the epoxy matrix. However, it can also be observed that the surface of MWCNTs is very slippery, which means the MWCNTs films are not saturated well by the epoxy matrix. The possible reason for the decrease in ILSS is that the MWCNTs films used in the composites are so compact and thick that it is difficult for the epoxy resin to penetrate in between, making the MWCNTs films insufficiently saturated. Therefore, contrary to expectation, the introduction of MWCNTs films would produce more defects in the composites and decrease the interlaminar shear property of the composites. Moreover, two different distinguished areas, area-A and area-B, can be ob-served in Fig.12(c). In area-A, MWCNTs can be discovered, but in area-B where glass fiber is placed, they cannot be seen. In fact, the existence of MWCNTs in area-B is covered up by the epoxy matrix because the glass fiber places on the matrix. Therefore, this can be viewed as if the epoxy matrix is reinforced by two separated phases, MWCNTs-D and glass fiber fabric, in a way similar to MWCNTs-C/GFRP. The interpenetration of MWCNTs and the glass fiber fabric does not come into force because MWCNTs in the film are prostrate and tangled up with each other. In addition, it is obvious from Fig.12(d) that MWCNTs are repelled by the glass fibers. All these factors result in decreased ILSS in MWCNTs-D/GF/EP laminates.

4 Conclusions

This article studies the interlaminar shear property of MWCNTs-modified GFRP. It is found that MWCNTs-A, MWCNTs-B and MWCNTs-E, which disperse directly in the epoxy matrix, increase the ILSS of GFRP. The highest ILSS of a composite is achieved with MWCNTs-E. However, although the orientated and film-shaped MWCNTs have improved their dispersion in the epoxy resin, the ILSS of the MWCNTs-C/GF/EP composite laminates, with orientated MWCNTs, and the MWCNTs-D/GF/EP with film-form MWCNTs, decrease dramatically because of the addition of MWCNTs-C and MWCNTs-D. This may be because of insufficient saturation of MWCNTs by the epoxy matrix and lack of the interpenetration of the MWCNTs and glass fiber fabric. The study on orientated MWCNTs and film-shaped MWCNTs-reinforced GF/EP composites is still in progress.

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